

Diffusion Coefficients in Aqueous Solutions of Ammonium Monovanadate at 25°C

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Received June 4, 2001

Differential diffusion coefficients of ammonium monovanadate in water at 25°C and at concentrations from 0.001 to 0.05 mol-dm⁻³, have been measured using a conductimetric cell and an automatic apparatus to follow diffusion. The cell uses an open-ended capillary method and a conductimetric technique is used to follow the diffusion process by measuring the resistance of solutions inside the capillaries at recorded times.

KEY WORDS: Diffusion; electrolytes; aqueous solutions; transport properties.

1. INTRODUCTION

Vanadium compounds are essential in many biochemical processes,^(1,2) although in high concentrations they may be toxic because of alterations of the enzyme activity responsible for phosphate metabolism. It has also been demonstrated that vanadium salts display insulinlike activity and may be used in the treatment of diabetes.⁽²⁾

No data for diffusion coefficients of ammonium monovanadate in water are reported in the literature, although such data are important for biochemical studies. The present paper is intended to fill this gap and reports experimental data at 25°C obtained by the open-ended capillary cell method previously described.⁽³⁾

The conductimetric technique presently used to follow the diffusion process by measuring the change with time of the ratio of electrical resistances of the electrolyte solutions in two vertically opposed capillaries has given us reasonably precise and accurate results.⁽⁴⁻⁹⁾

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2. EXPERIMENTAL

The apparatus assembled for use with the open-ended capillary cell in this laboratory is essentially the same as previously reported.⁽³⁾ The cell has two vertical capillaries, each closed at one end by a platinum electrode and positioned one above the other with the open ends, separated by a distance of about 14 mm.

The upper and lower tubes, initially filled with solutions of concentrations $0.75\ c$ and $1.25\ c$, respectively, are surrounded with a solution of concentration c . This ambient solution is contained in a glass tank $200 \times 140 \times 60$ mm immersed in a thermostat at 25°C . The tank is divided internally by Perspex sheets and a glass stirrer creates a slow lateral flow of ambient solution across the open ends of the capillaries. Experimental conditions are such that the concentration at each of the open ends is equal to the ambient solution value c : that is, the physical length of the capillary tube coincides with the diffusion path. In other words, required boundary conditions described in the literature⁽³⁾ to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl effect⁽³⁾ is reduced to negligible proportions. In a manually operated apparatus, diffusion is followed by measuring the ratio $w = R_t/R_b$ of resistances R_t and R_b of the upper and lower tubes by an alternating current transformer bridge. In an automatic apparatus, w is measured by a Solartron digital voltmeter (DVM) 7061 with $6\frac{1}{2}$ digits. A power source (Bradley Electronics Model 232) supplies a 30-V sinusoidal signal at 4 kHz (stable to within 0.1 mV) to a potential divider that applies a 250-mV signal to the platinum electrodes at the top and bottom capillaries. By measuring the voltages V' and V'' from top and bottom electrodes to a central electrode at ground potential, in a fraction of a second, the DVM calculates w .

In order to measure the differential diffusion coefficient D at a given concentration c , a "top" solution of concentration $0.75\ c$ and a "bottom" solution of concentration $1.25\ c$ are prepared, each in a 2-L volumetric flask. The "bulk" solution of concentration c is prepared by mixing 1-L of "top" solution with 1-L of "bottom" solution, measured accurately. The ammonium monovanadate solutions were prepared from *pro analysi* Merck reagent. To increase the dissolution rate of this salt in water, we raise the temperature of the solutions to 80°C and then allow them to cool to 25°C . The glass tank and the two capillaries are filled with c solution, immersed in the thermostat, and allowed to come to thermal equilibrium. The resistance ratio $w = w_\infty$ measured under these conditions (with solutions in both capillaries at concentration c accurately gives the quantity $\tau_\infty = 10^4/(1 + w_\infty)$.

The capillaries are filled with the "top" and "bottom" solutions, which are then allowed to diffuse into the "bulk" solution. Resistance ratio readings are recorded at intervals, beginning 1000 min after the start of the experiment, to determine the quantity $\tau = 10^4/(1 + w)$ as τ approaches τ_∞ . The diffusion coefficient is evaluated using a linear least-squares procedure to fit the data and, finally, an iterative process using 20 terms of the series expansion of Fick's second law

Table I. Diffusion Experiments with 0.01 mol-dm⁻³ NH₄VO₃ in Aqueous Solutions at 25°C

| $10^9 D^a$ | τ_∞ |
|------------|---------------|
| 1.130 | 4999.8 |
| 1.140 | 5001.0 |
| 1.134 | 4999.8 |

^aD in m²-s⁻¹. Mean of three experiments: $D_{av} = 1.135 \times 10^{-9}$ m²-s⁻¹. Standard deviation of the mean: $S_{Dav} = 0.003 \times 10^{-9}$.

for the present boundary conditions. The theory developed for the cell has been described earlier.⁽³⁾

3. RESULTS AND DISCUSSION

The results of diffusion experiments for solutions of 0.01 mol-dm⁻³ NH₄VO₃ at 25°C are shown in Table I. They are in good agreement and indicate the precision of the method for measuring differential diffusion coefficients. Measurements for 0.1 mol-dm⁻³ KCl solutions by this method agree with those of Miller within 0.1%.⁽⁹⁾

Table II shows the results with ammonium monovanadate solutions from 1×10^{-3} to 5×10^{-2} mol-dm⁻³ at 25°C. Results are averages of three experiments performed on consecutive days. Reproducibility of the results is good, as shown by the standard deviation of the mean, S_{Dav} . Previous papers reporting data obtained with our conductimetric cell support our view that the inaccuracy of our

Table II. Diffusion Coefficients of NH₄VO₃ in Aqueous Solutions at 25°C at Several Concentrations

| c^a | $10^9 D_{av}^b$ | τ_∞ | $10^9 S_{Dav}^c$ |
|-------|-----------------|---------------|------------------|
| 0.001 | 1.264 | 5000.5 | 0.018 |
| 0.005 | 1.174 | 4999.8 | 0.009 |
| 0.010 | 1.135 | 5000.0 | 0.003 |
| 0.020 | 1.116 | 5010.0 | 0.006 |
| 0.030 | 1.110 | 5011.1 | 0.010 |
| 0.050 | 1.090 | 4995.5 | 0.008 |

^amol-dm⁻³.

^b D_{av} , mean value of D in three experiments, m²-s⁻¹.

^c S_{Dav} , standard deviation of D_{av} .

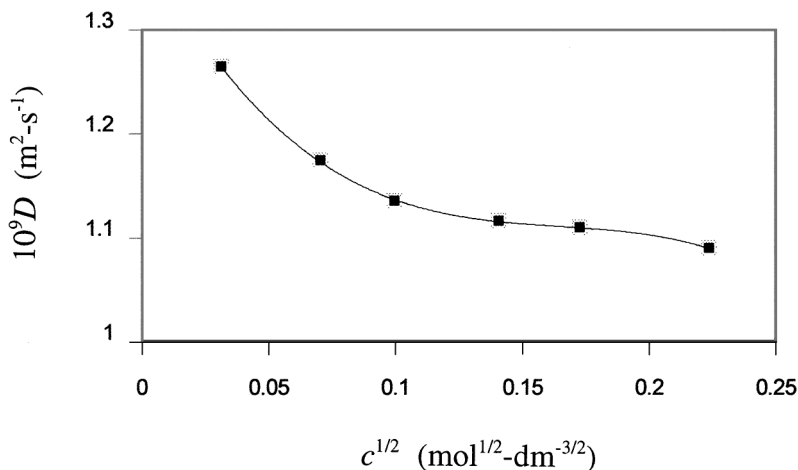


Fig. 1. Experimental diffusion coefficients of NH_4VO_3 in water at 25°C .

results should not be much larger than the imprecision; that is, we believe that the uncertainty is not much larger than 1–2%.

Fitting the data in Table II to the empirical equation,

$$10^9 D = 1.388 - 4.715\sqrt{c} + 27.66c - 55.96c^{3/2} \quad (1)$$

with D in $\text{m}^2\text{-s}^{-1}$ and c in mol-dm^{-3} , we obtain the curve shown in Fig. 1.

Figure 1 shows the diffusion behavior of this electrolyte in aqueous solutions fitted with this equation. The decrease of the diffusion coefficient with increasing concentration may be interpreted on the basis of new species resulting from the hydrolysis of the salt. In fact, the literature^(1,2,10–12) and the analysis of solutions by ^{51}N nuclear magnetic resonance (NMR), performed in this department in the range of concentrations studied ($1 \times 10^{-3} \text{ mol-dm}^{-3} \leq c \leq 0.05 \text{ mol-dm}^{-3}$) where the pH varied between 6.8 and 7.2, show that $\text{V}_4\text{O}_{12}^{4-}$ predominates in these circumstances, its concentration increasing as the concentration of the salt NH_4VO_3 increases. The decrease of $D_{\text{NH}_4\text{VO}_3}$ with concentration, shown in Fig. 1, may be explained by assuming that $\text{V}_4\text{O}_{12}^{4-}$ has a lower mobility than other anions probably a mixture of $\text{V}_x\text{O}_{3x}^{x-}$ anions, possibly including VO_3^- because of its size. The eventual formation of ion pairs, increasing with concentration, also may contribute to the decrease of $D_{\text{NH}_4\text{VO}_3}$ with increasing concentration.

ACKNOWLEDGMENT

We are grateful to Dr M. L. D. Ramos for NMR measurements and her valuable comments on the species in these solutions.

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